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(54) **Elastomeric insulating materials free of asbestos for the internal walls of rocket engines.**

(57) The asbestos-free insulating materials contain 100 parts by weight of a cross-linked elastomeric polymer and around 10 and 100 (preferably between 15 and 75) parts by weight of organic fibers chosen from among cotton flocks, sisal, and a combination of these two fibers. These materials have a substantial resistance to erosion and can be designed to have desired thermal, mechanical or other properties. The organic fibers play the part of a low-density carbonizable filler. Other ingredients such as silica, a phenolic resin, polybutadiene, etc., improve the useful properties of the insulating materials.

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ELASTOMERIC INSULATING MATERIALS FREE OF ASBESTOS FOR THE INTERNAL WALLS OF ROCKET ENGINES.

The present invention concerns elastomeric insulating materials free of asbestos, especially designed to insulate the internal walls of rocket engines against the hot and gaseous combustion products emitted by the propergol. More particularly, it concerns insulating materials of this type that contain, as low-density filler, carbonizable organic fibers.

The requirements imposed by the satisfactory insulation of a rocket engine depend on the mass flow in the surface of application and the duration of combustion of the rocket engine. In order to satisfy these requirements in rocket engines, elastomeric insulating materials containing asbestos have long been used. However, it is very desirable to avoid the highly toxic collateral effects on the environment from the use of asbestos.

European patent 0020.273 describes an elastomeric heat shield based on silica, free of asbestos. Besides silica, the filler (50 to 150 parts by weight per 100 parts of elastomer) contains up to 15 parts by weight of aromatic polyamide fibers. Because of the relatively high cost of these fibers, there has long been felt the need for a filler which contains less costly organic fibers and which can be used without these relatively high contents of silica.

The elastomeric insulating material free of asbestos for rocket engines according to the invention, which contains a cross-linked elastomeric polymer and carbonizable organic fibers, is characterized in that the organic fibers are cotton flocks, sisal, or a combination of cotton flocks and sisal, and in that the content of organic fibers is between around 10 and around 100 parts by weight per 100 parts by weight of elastomer.

The cotton flocks are short cotton fibers obtained by shredding cotton fabrics. They can come from the textile and the garment industries. One obtains low-quality cotton flocks by starting with worn fabrics. Sisal is a tough fiber obtained from plants of the Amaryllidaceae family.

The elastomeric insulating material according to the invention preferably contains between around 15 and 75 parts by weight of carbonizable organic fibers per 100 parts of cross-linkable elastomer.

The cotton flocks constitute the preferred carbonizable organic fibers. According to the invention, the density of the cotton flocks is preferably between around 1.5 and 1.7 g per cubic centimeter with nominal mesh dimensions from 1.8 mm to 75 μm. The diameters of the fibers

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are preferably between around 15 and 20 microns, and it is preferable to use white or nondyed fibers.

The use of cotton flocks in the insulating materials according to the invention results in materials having an appreciable resistance to erosion, in some cases better than that of similar elastomeric insulating materials which contain asbestos.

For example, the speed of erosion can be as low as 0.4572 mm/s at flow rates of 0.1067 bar/s, compared to 0.7112 mm/s for materials containing asbestos at this flow rate.

For convenience, the expression "percent by weight of the elastomeric polymer" shall be abbreviated hereafter as "phr."

One also preferably uses a mineral filler in the insulating materials of the invention. A typical example of mineral filler is silica, at a content between around 5 and 80 phr and preferably between around 10 and 50 phr. One can also use other well-known mineral fillers: one of them which is preferred is antimony oxide, which one can use as an ignition retarder for the insulating materials of the invention. The antimony oxide is preferably used in a content between around 50 and 60 phr, and even more preferably between around 10 and 35 phr.

Among the cross-linkable elastomeric polymers suited to the invention one can mention polymers based on ethylene propylene diene monomer (EPDM) and chlorosulfonated polymers of polyethylene; these two polymers are commercially available. However, the invention is not in any way limited to a particular elastomer, yet it has to be cross-linkable.

The chlorosulfonated polymers used according to the invention are preferably polymerized by a starch/magnesia polymerization system. The starch in this system advantageously acts as a cooling agent, by decomposing in water which has a high heat of evaporation. One preferably uses between around 10 and 150 phr of starch with the chlorosulfonated polyethylenes and even more preferably between around 20 and 60 phr.

In these embodiments, one uses the magnesium oxide between around 1 and 15 phr and preferably between around 1 and 10 phr.

Besides the starch/magnesia polymerization system, one preferably uses an accelerator with the chlorosulfonated polyethylene polymers. Sulfur accelerators are preferred. As a commercially available example, one can mention TETRONE A from Dupont. The accelerator is normally used in content between around 0.5 and 5 phr.

EPDM polymers with the following properties are preferred:

Density, g/cc	0.85 to 0.865
Mooney, ML-4 @ 100°C	25 to 60
Point of brittleness, °C	-68°
Hardness, shore A	30 to 90
Tensile strength	34.45 bars to
(gum-stock)	68.948 bars.

The specific adapted EPDM polymers are those sold under the names Hypalon LD-999 by Dupont, Nordel (R) by Dupont, Royalene (R) 100, by Uniroyal, Epsyn (R) 4506 by Copolymere and Vistalon (R) 2504 by Exxon.

The EPDM polymer is preferably polymerized with a peroxide such as dicumyl peroxide or a t-butyl peroxy compound. The compounds are used with the EPDM in a content between around 0.5 and 5 phr.

Besides the organic fibers and the mineral particles, the insulating materials can contain other organic additives to improve the insulating properties. For example, one can use chlorinated organic compounds for ignition retardation with antimony oxide or hydrated alumina to further improve the resistance to ignition of the EPDM insulating materials. The chlorinated hydrocarbons such as Dechlorane (R) are effective for this purpose. The ignition retarder is used in concentrations between around 10 and 80 phr and preferably between 15 and 65 phr.

Liquid polybutadiene is another organic material which is used in adapted manner in the elastomeric materials of the invention. Liquid polybutadiene can increase the resistance to erosion, as well as reduce the rigidity in the EPDM insulating materials of the invention. The typical content of liquid polybutadiene is around 1 to 50 phr and preferably 5 to 90 phr. One can mention as an example of liquid polybutadiene Butarez NF from Phillips Petroleum.

One can further use particulate organic products such as those derived from phenolic resins as replacement of all or some of the silica in order to limit the visibility of the combustion products of the insulator; the particulate phenolic resin is used in doses between around 30 and 150 phr to increase the formation of bone black and improve the resistance to erosion, especially in insulating materials based on chlorosulfonated polyethylene of the invention. As an example of phenolic resins, one can mention the product Resinox (R) of Monsanto.

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The elastomeric insulating materials of the invention can be flexible or rigid and the particulate level can be adjusted to modify the modulus according to the particular application requirements.

In the present specification, the term "insulation of the walls of the mold" refers to the material bound to the inner wall of the mold of the rocket engine to protect it against hot combustion products produced by this engine. For applications of this type, compositions A, B, C, D of Table V constitute examples of suitable materials according to the invention.

The term "insulation of the flow channel" refers to the material used to protect the inner wall of the flow channel of a rocket, that is, the channel which transports the combustion products to the nozzle of the rocket, if the nozzle is not connected directly to the rocket engine. The lining of the flow channel protects this channel against the hot combustion gases of the rocket engine. Composition C of TABLE V is an example of a suitable material according to the invention for coating the flow channels.

Tables A, B and C below give examples of formulations of insulating materials according to the invention.

One may advantageously select specific polymerized elastomeric insulators to achieve an elevated resistance to erosion which is comparable to or better than their analogues containing asbestos, as well as have the desired thermal and mechanical properties and the bonding capacity to standard propellants and to bonding agents.

TABLE A

Ingredients	Parts by weight
Chlorosulfonated polyethylene	100
Starch	30-50
Magnesia	1-10
Phenolic resin	80-20
Cotton flocks	30-50
Accelerator	0.5-5

The insulating materials of this embodiment A have a high resistance to erosion.

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TABLE B

Ingredients	Parts by weight
Chlorosulfonated polyethylene	100
Magnesium oxide	1-10
Accelerator	0.5-5
Cotton flocks	30-80
Starch	30-50
Hydrated silica	10-30

The insulating materials of this embodiment B have a good resistance to erosion and, advantageously, do not adsorb significant quantities of low-polarity plasticizer from the propellants which contain them.

TABLE C

Ingredients	Parts by weight
EPDM	100
Cross linking agent	1-5
Organic ignition retarding product	20-60
Mineral ignition retarding product	10-40
Cotton flocks	10-60
Liquid polybutadiene	0-15

The insulators according to this embodiment C are especially adapted to insulating the walls of the mold or the flow channel by reason of their physical and thermal properties and their ability to retard ignition.

TABLE D

Ingredients	Parts by weight
EPDM	100
Cross linking agent	1-5
Cotton flocks	20-80
Hydrated silica	10-30

The insulators of this embodiment D of the invention are preferably used as low-density insulators having excellent mechanical, thermal, and abrasion resistance properties, as well as assembly strength.

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Preparation of the precursors of the insulation materials of the invention is done at temperatures lower than the polymerization temperatures of the elastomer and permits losses of ingredients.

Normally, these temperatures are lower than around 121°C for EPDM and lower than around 93.3°C or even 65.6°C for the chlorinated polyethylene compounds. One can prepare the compositions in classical mixing and grinding layouts.

The insulating material of the invention can be applied to the engine molds by wrapping rolled sheets of the insulator about an inflatable mandrel known as a "bladder mandrel." The mandrel is then inserted into the mold and inflated in order to force the insulator against this mold, where it is compacted under pressure. The assembly, with the mandrel inflated, is then placed in an oven where the insulator is polymerized. One usually employs oven temperatures of 149°C to 177°C. In the case of EPDM polymerized with peroxide, one usually needs a minimum temperature of around 154°C. Once the insulator is polymerized, the mandrel is removed, and one has an insulated mold. It may be advantageous to use "primary layers" on a metal mold to improve the bond with the elastomeric insulator. One can use primary layers such as Chemlok 233 or a combination of Chemlok 205 and 234 B (products from the Hughson Division of Lord Corporation).

Alternatively to the use of the inflatable mandrel technique described above, the insulator can be molded in metal die plates for subsequent bonding to the mold of the rocket engine.

Moreover, the insulating formulas can be adapted to a process which utilizes a ribbon format for the insulation of precision rocket engines.

The following examples will illustrate the various aspects of the invention, without thereby limiting its scope, yet demonstrating the different practical aspects.

Example 1

The following formulation (Table I) and the methods are suitable to obtaining an elastomeric insulation material according to the invention. This material is intended to insulate molds.

TABLE I

Components	Ingredients	Phr	Wt. %
1	chlorosulfonated polyethylene (a)	100	45.87
2	magnesium oxide (b)	6.0	2.75
3	dipentamethylene thiurum hexasulfide (c)	2.0	0.92
4	cotton flocks (d)	50.0	22.94
5	corn starch (e)	40.0	18.35
6	hydrated silica (f)	20.0	9.17

(a) Hypalon LD-999 E.I. Dupont

(b) Activated powder, C.P. Hall Co.

(c) Tetron A from E. I. Dupont

(d) Grade 4128 from Danberg Chemical Co.

(e) American Maize Products Co.

(f) HiSil 233 from PPG Industries Inc.

A first insulator batch is prepared from the components of Table I on a roll mill with cooling (Farrel Differential Roll Mill) as follows, at temperatures below 23.3°C:

Order of adding	Component	Length of grinding (g)
First	1	3-5 minutes
Second	2	2-3 minutes
Third	3	2-3 minutes
Fourth	5	5-6 minutes
Fifth	6	5-6 minutes
Sixth	4	13-15 minutes

(g) includes the time for adding the ingredients.

A second insulator batch is composed as follows, starting from the products of Table I, in a Baker-Perkins mixer, at a final temperature below around 65.6°C.

Order of adding		Component	Length of grinding (g)
First	1	10	
Second	6	12	
Third	4	12	
Fourth	5	5	
Fifth	2 and 3	15	

Once each of the batches has been mixed and cooled to room temperature, it is kept in polyethylene bags to avoid any contamination.

The above components, utilized according to one of the two methods followed by a polymerization at 152.7°C for 30 minutes, present the following properties:

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PHYSICAL PROPERTIES

	Laboratory stage mixing	Industrial stage mixing
1. Tensile properties (ASTM D.412-66 after 30 minutes at 152°c)		
(i) final tensile strength (bars)		
with fibers	136.97	117.13
against fibers	101.69	
(ii) final elongation, percent		
with fibers	30	40
against fibers	80	
2. Hardness, Shore A (ASTM D-314-28)	95	
3. Density g/cm3	1.378	1.362

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The polymerized elastomer of this example is suitable as bond for use with propellants for rocket engines containing hydroxy or carboxy-terminal polybutadiene. Because of its rigidity, it is advantageously used to insulate the walls of molds or, because of its low affinity for many plasticizers, as a barrier film for other insulators.

In order to achieve a better solidification, it is recommended to do a post-polymerization for 10 hours at 121°C, followed by sandblasting, then cleaning with solvent (chlorethylene). Specific applications may require an investigation of the compatibility of the propellant/insulator bond.

Example 2

The following formulation (Table II) and methods are adapted to make elastomeric materials according to the invention for insulating the molds of rocket engines.

TABLE II

Components	Ingredients	Phr	Wt. %
1	chlorosulfonated polyethylene (a)	100	34.73
2	magnesium oxide (b)	6.0	2.08
3	starch (c)	40	13.89
4	cotton flocks (d)	40	13.89
5	phenolic resin (e)	100	34.72
6	dipentamethylene thiurium hexasulfide	2.0	0.69
			100.00

(a) Hypalon LD-999 from E. I. Dupont de Nemours

(b) Activated powder, C.P. Hall Co.

(c) Corn starch, American Maize Products Co.

(d) Grade 4128 from Danberg Chemical Co.

(e) Resinox RC 755 from Monsanto

(f) Sulfad from R. T. Vanderbilt or Tetrone A from E. I. Dupont de Nemours.

From the components of Table II, one prepares a batch of insulating elastomer in a roll mill with cooling, at temperatures below 93.3°C, as follows:

Order of adding grinding (g)		Component	Length of
First	1	3--5 minutes	
Second	2	2--3 minutes	
Third	6	2--3 minutes	
Fourth	3	5--6 minutes	
Fifth	5	6--9 minutes	
Sixth	4	13--15 minutes	

(g) includes the time for adding the ingredients.

Once this batch has been mixed and cooled to room temperature, it is kept in polyethylene bags to prevent any contamination.

One obtains the following properties with the components of this example 2, polymerized at a temperature of 152.7°C for 30 minutes:

Physical properties

1. Tensile properties
   (ASTM D-412-66 after 10
   minutes at 171°c)   Mixed in the laboratory
   Final tensile strength (bars)
      with the fibers   193.67
   Final elongation, percent
      with the fibers   20
2. Shore hardness A (ASTM D-314-28)   95
3. Density g/cm3   1.306

The polymerized elastomer of this example is suitable for use in rocket engines with propellants based on polybutadiene bonded to the hydroxy or carboxy termination.

Because of its rigidity, this elastomer is used for insulation bonded to the mold walls or as insulator of the flow channel. A post-polymerization of 10 hours at 121°C is recommended. Specific applications may require investigation of the compatibility of the propellant/insulation bond.

Example 3

One uses the formulation given in Table III below to make an elastomeric insulating material according to the invention.

TABLE III

Components	Ingredients	Phr	Wt. %
1	EPDM (a)	100.00	51.95
2	2,5-dimethyl-2,5-di-(t-butylperoxy) hexane (b)	2.5	1.30
3	ignition retarder (c)	40.0	20.78
4	antimony oxide (d)	20.0	10.39
5	cotton flocks (e)	20.0	10.39
6	linear polybutadiene (f)	10.0	5.19
		100.0	

(a) Nordel 1040 from E. I. Dupont

(b) Varox from R. T. Vanderbilt

(c) Dechlorane Plus 515 from Hooker Chemical

(d) Mil-A-51312, Harshaw Chemical Co.

(e) Grade 4128 from Danberg Chemical Company

(f) Butarez N. F. from Phillips Petroleum Co.

Using the components from Table III, one composes as follows a first batch of insulation precursor, at temperatures below 121°C, in a roll mill with cooling:

Order of adding	Component	Length of grinding (g)
First	1	1--3 minutes
Second	2	2--3 minutes
Third	3	10--12 minutes
Fourth	4	5--6 minutes
Fifth	6	6--9 minutes
Sixth	5	13--15 minutes

(g) includes the time for adding the ingredients.

One composes as follows a second batch in a Baker-Perkins mixer, from the components of Table III, at temperatures below 121°C.

Order of adding	Component	Length of mixing (minimum)
First	1	10 minutes
Second	3	15 minutes
Third	4	5 minutes
Fourth	6	until well incorporated
Fifth (1)	5	16 minutes
Sixth	2	15 minutes

(1) the cotton flocks can be added in small quantities to facilitate their incorporation in the mixture.

One obtains the following physical properties by polymerizing one of the components of this example 3 at a temperature of 171°C for 30 minutes:

Physical properties

1. Tensile properties
   (ASTM D-412-66 after 10   Mixed in the laboratory
   minutes at 171°c)
   Final tensile strength
   (bars)   33.347
        with the fibers
   Final elongation, percent   63
        with the fibers
2. Shore hardness A (ASTM D-314-28)   70
3. Density g/cm3   1.143

The elastomer polymerized according to this example can be used for floats, the coating of molds or insulating materials for rocket engines. A post-polymerization for 10 hours at 121°C is recommended. Specific applications may require an investigation of the compatibility with propellant formulations. For adhesion to steel or to the polymerized elastomer itself, one can use adhesives based on epoxy and adhesives based on polybutadiene. Furthermore, in this case, one can use the nonpolymerized elastomer as the bond.

Example 4

The following formulation (Table IV) and the following methods are suitable for making an elastomeric insulation material according to the invention.

TABLE IV

Components	Ingredients	Phr	Wt. %
1	EPDM (a)	100.00	57.971
2	2,5-dimethyl-2,5-di(t-butylperoxy) hexane (b)	2.5	1.449
3	cotton flocks (c)	50.0	28.986
4	hydrated silica (d)	20.0	11.594
			100.00

(a) Nordel 1040 Dupont

(b) Varox from R. T. Vanderbilt

(c) Grade 4128 from Danberg Chemical Co.

(d) HiSil 233 from PPG Industries Inc.

One prepares a first batch from the components of Table IV on a roll mill with cooling (Farrel Differential Roll Mill) at temperatures below 93.3°C:

Order of adding	Component	Length of grinding (g)
First	1	1--3 minutes
Second	2	2--3 minutes
Third	3	10--12 minutes
Fourth	4	13--15 minutes

(g) includes the time for adding the ingredients.

One prepares a second batch from the components of Table IV in a Baker-Perkins mixer, at a final temperature less than 93.3°C.

Order of adding	Component	Length of grinding (g)
First	1	10 minutes
Second (1)	3	12 minutes
Third (1)	4	30 minutes
Fourth	2	15 minutes

(1) the HiSil 233 and the cotton flocks are added little by little to facilitate their incorporation in the mixture.

One obtains the following physical properties by polymerizing one of the components of example 4 at temperatures of around 171°C for 30 minutes:

Physical properties

1. Tensile properties

(ASTM D-412-66 after 10	Mixed in the laboratory
minutes at 171°C)	
Final tensile strength (bars)	44.23
with the fibers	
against the fibers	
Final elongation, percent	40
with the fibers	
against the fibers	

2. Shore hardness A (ASTM D-314-28)   80
3. Density g/cm3   1.060

The polymerized elastomer of this example can be used as float, mold coating or insulating material for rocket engine molds. With this elastomer, one can use both propellants of polybutadiene bonded to the hydroxy termination and those bonded to the carboxy termination. Among the suitable adhesives for bonding the elastomer to steel or to itself, one can mention the epoxies and the adhesives based on Butarez CTL. The formulation is bonded to itself during the polymerization. Before coming into contact with the propellant, a post-polymerization of 10 hours at 121°C is recommended. Specific propellant formulations may require investigation of the compatibility of the insulator/propellant bond.

Experimental results

Table V below illustrates the results which can be obtained from polymerized elastomeric materials fabricated according to the invention and the compositions of the prior art, containing asbestos.

In Table V, formulation A is obtained by the methods of example 3, formulation B by those of example 4, formulation C by those of example 2 and formulation D by

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those of example 1. Formulations E through H correspond to classical elastomeric materials used in the molds of rocket engines and containing asbestos.

TABLE V

PROPERTIES OF EROSION, MECHANICAL AND THERMAL PROPERTIES, DENSITY OF INSULATORS ACCORDING TO THE EXAMPLES, COMPARED TO THOSE OF INSULATORS CONTAINING ASBESTOS

Ingredients, phr	A	B	C	D	E	F	G	H
EPDM (a)	100.0	100.0			100.0	100.0	100.0	—
2,5-dimethyl-2,5 (di-t-butyl-peroxy)-hexane (b)	2.5	2.5			2.5	2.5	7.5	
Ignition retardant (c)	40.0				40.0	40.0		
Antimony oxide	20.0				20.0	20.0		
Polybutadiene (d)	10.0				10.0			
Cotton flocks	20.0	50.0	40.0	50.0				
Silica (e)		20.0		20.0				
Chlorosulfonated polyethylene (f)			100.0	100.0				
Magnesia			6.0	6.0				
Starch			40.0	40.0				
Dipentamethylene thiurum hexasulfide (g)			2.0	2.0				
Phenolic resin (h)			100.0					
Asbestos					20.0	20.0		
Phenolic resin						100.0	100.0	
Asbestos felt								300.0
Polybutadiene (j)							10.0	
Erosion/Decomposition								
mm/s								
0.0168 bar/s	0.254	0.2159	0.1778	0.254	0.2794	0.3048	0.1778	
0.0097 bars/s	0.3302	0.228-02794	0.127	0.330	0.2794	0.355	0.9724	
10.27 bars/s	1.016	10.16	0.4572	1.5748	1.4224	-	0.7112	0.7112

Mechanical properties
(25°C, 50.8 cm/min X Head)

m, %	63	40	20	30	63	284	29	
m, bar	33.34	44.23	186.719	136.97	24.80	31.35	157.02	2620
Density, g/cm3	1.143	1.071	1.265	1.362		1.184	1.273	1.688
Hardness Rex	70	80	95	95	80	75	85	100

Thermal properties

Expansion,
cm/cm deg C x 10^{-5}

0	-13.5	-14.3	-16.5	-15.6	---	-12.72	---	---
1	-3.83	-4.16	-9.6	-8.5	-4.4	-2.6	---	-2.7

Conductivity

W/M°C	0.225	0.173	0.19	0.2596	0.2249	0.9077	0.346	0.227-0.519
Tg deg C	-58.8	-52.2	-16.1	-10		-57.8		25

* Apparatus of 5.08 cm   ** Test engine, of 15.24 cm

(a) Nordel 1040[R]
(b) Varox[R]
(c) Dechlorane Plus[R]
(d) Butarez NF[R]
(e) HiSil 233[R]
(f) Hypalon LD-999[R]
(g) Sulfads[R]
(h) Resinox RC 755[R]
(i) Plastibest 20[R]
(j) Butarez CTL II[R]

Table VI summarizes the properties of elastomers obtained according to the methods of example 3 as compared to similar materials containing asbestos. The formulations summarized in Table VI, i.e., A1, A2, A3, A4, A5 and A6, are variants of formulations A of Table V.

TABLE VI

Ingredient, phr	A1	E1	A2	A3	A4	A5	E2	A6
EPDM (a)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
2,5-dimethyl-2,5-(di-t-butyl-peroxy hexane) (b)	2.5	2.5	2.5	2.5	2.5	7.5	2.5	2.5
Sisal, fibers of 635 mm	20.0	---	---	80.0	---	---	---	---
Cotton flocks	---	---	20.0	---	20.0	20.0	---	---
Antimony oxide	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
Ignition retardant (c)	40.0	40.0	40.0	40.0	40.0	40.0	40.0	40.0
Polybutadiene (d)	10.0	10.0	10.0	---	---	10.0	---	10.0
Asbestos	---	20.0	---	---	---	---	20.0	---
Cotton flocks+ A-172 (silane coupling agent)	---	---	---	---	---	---	---	20.0
Erosion/Decomposition (mm/s)	0.2794	0.3048	0.254	0.3556	0.4318	0.190	0.2794	0.2286
Mechanical properties (25°C, 50.8 cm/min X Head)								
m, %	40	284	63	20	60	40	63	73
m, bar	21.56	31.35	33.35	69.08	27.73	60.49	24.80	40.79

(a) Nordel 1040[R]
(b) Varox[R]
(c) Dechlorane Plus[R]
(d) Butarez NF[R]

Table VII summarizes the properties of elastomers obtained by the methods of example 4. The formulations summarized in Table VII, that is, B1, B2, B3, B4 and B5, are variants of formulation B of Table V.

TABLE VII

Ingredient, phr	B1	B2	B3	B4	B5
EPDM (a)	100.0	100.0	100.0	100.0	100.0
2,5-dimethyl-2,5 (di-t-butylperoxy) hexane (b)	2.5	2.5	2.5	2.5	2.5
Silica (c)	35.0	35.0	20.0	20.0	40.0
Cotton flocks	----	----	10.0	50.0	50.0
Acetylene black (100% comp.)	0.5	----			
Di-beta-naphthyl-p-phenylene diamine sym (d)		3.0			
Erosion/Decomposition (mm/s)*	0.304	0.381	0.279	0.216	0.210
Mechanical properties (25°C, 50.8 cm/min X Head)					
m, %	845	1258	540	40	30
m, bar	119.00	55.94	48.02	44.23	61.87

*0.0168 bar/s
(a) Nordel 1040[R]
(b) Varox[R]
(c) HiSil 233[R]
(d) Agerite White[R]

Table VII summarizes the properties of elastomers obtained by example 2 as compared to analogous compositions containing asbestos. The formulations summarized in Table VIII, that is, C1, C2, C3, C4, C5 and C6, are variants of formulation C of Table V.

TABLE VIII

Ingredient, phr	C1	C2	C3	C4	C5	C6	G	E	H
Chlorosulfonated polyethylene (a)	100.0	100.0	100.0	100.0	100.0	100.0			
Magnesia	6.0	4.0	6.0	6.0	6.0	6.0			
Dipentamethylene thiurum hexasulfide (b)	2.0	2.0	2.0	2.0	2.0	2.0			
Corn starch	40.0	10.0	40.0	100.0	40.0	40.0			
Cotton flocks	40.0	---	40.0	40.0	40.0	---			
Phenolic resin	100.0	---	60.0	60.0	100.0	100.0			
Sisal, fibers of 6.35 mm					60.0	40.0			
EPDM (d)							100.0	100.0	
2,5 dimethyl-2,5-di (t-butyl-peroxy) hexane (e)							7.5	2.5	
Asbestos							100.0	20.0	
Linear polybutadiene (f)							10.0	---	
Antimony oxide								20.0	
Ignition retardant (g)									40.0
Asbestos felt									300
Phenolic resin									100
Erosion/Decomposition									
Rate, mm/s at 0.0168 bar/s	0.170	---	0.203	0.183	0.228	0.305	---	0.279	0.178
Mechanical properties									
(25°C, 50.8 cm/min, X Head)									
m, %	20	475	50	10	10	10	29	63	1.15
m, bar	193.78	207.11	135.87	167.15	215.79	207.94	157.02	24.80	3 100.5

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(a) Hypalon LD-999$^{(R)}$
(b) Tetron A$^{(R)}$
(c) Resinox 755$^{(R)}$
(d) Nordel 1040$^{(R)}$
(e) Varox$^{(R)}$
(f) Butarez CTL II$^{(R)}$
(g) Dechlorane Plus$^{(R)}$

Table IX summarizes the test results for absorption of plasticizers by the elastomers according to the invention as compared to analogous formulations containing asbestos; formulations A, B, C, D, and F are found in Table V.

TABLE IX

Insulator	Test temperature, °C	Absorption of plasticizer after 120 hours, percent			
		CLO[1]	IDP[2]	DOA[3]	3GH[4]
F	25.0	67	119	10	42
	62.7	192	130	34	60
A	25.0	95	88	-1.7	15
	62.7	124	182	-2.7	57
B	25.0	62	68	4	23
	62.7	125	86	8	43
C	25		4		5
	62.7		16		22
D	25.0	1.5	7	8	9
	62.7	9	21	28	29

Increase of polarity

(1) Light oil Circo[R]
(2) Isodecyl pelargonate
(3) Dioctyl adipate
(4) Flexol 3 GH[R]

Table X summarizes the results of the bonding of elastomeric materials according to the invention (A, B, C and D of Table V) in presence and in absence of A-128, a coating material prepared as in example 5 (Table XIII), to a standard propellant composition containing, as the bond, a polybutadiene with a hydroxy termination. Also given are the results for the bonding of composition H (Table V).

TABLE X

Insulation system	Test temperature °C	Tensile strength of the bond (bar)		
		≠ 1	≠ 2	≠ 3
D	− 54	24,32 (CP)	28,45 (CP)	28,66 (CP)
	25	3,03 (M)	1,24 (A)	3,03 (M)
	73,8	1,44 (A)	1,309 (A)	0,689 (A)
D + A − 128	− 54	33,69 (CP)	26,25 (CP)	———
	25	6,54 (CP)	5,30 (CP)	7,37 (CP)
	73,8	4,54 (CP)	4,48 (CP)	4,75 (CP)
A	− 54	32,72 (CP)	38,99 (CP)	33,69 (CP)
	25	6,13 (CP)	6,89 (CP)	6,47 (CP)
	73,8	5,58 (CP)	5,10 (CP)	4,75 (CP)
A + A − 128	− 54	33,41 (CP)	26,04 (CP)	———
	25	8,90 (CP)	8,06 (CP)	7,37 (CP)
	73,8	4,68 (M)	5,85 (CP)	4,82 (M)
C	− 54	19,84 (A)	18,46 (A)	
	25	1,378 (A)	0,758 (A)	1,24 (A)
	73,8	———	0,689 (A)	0,344 (A)
C + A − 128	− 54	38,51 (CP)	33,28 (CP)	38,03 (CP)
	25	4,82 (CP)	7,58 (CP)	7,23 (CP)
	73,8	4,61 (CP)	5,92 (CP)	4,48 (CP)
D	− 54	24,66 (A)	27,69 (A)	19,43 (A)
	25	1,65 (A)	1,93 (A)	2,96 (A)
	73,8	1,86 (A)	———	1,86 (A)
D + A − 128	− 54	36,79 (CP)	33,41 (CP)	38,92 (CP)
	25	6,96 (CP)	6,96 (CP)	6,75 (CP)
	73,8	4,90 (CP)	4,68 (CP)	4,75 (CP)
H	− 54	29,21 (M)	35,83 (M)	———
	25	6,75	6,13	6,96
	73,8	4,89 (M)	5,10 (M)	5,10 (M)

A = no adhesiveness in the bond

CP = lack of cohesion in the propellant

M = lack in both the bond and the propellant

<u>Example 5</u>:

This example illustrates the use of elastomeric compositions per the invention in the specific application of stress relief lining (SRL) for grain type propellants with terminal combustion or internal combustion with strong stresses. The principle of the SRL is to break the normal stresses for the propellant grains bonded to the mold in a rocket engine, into small columns of stresses which independently support a triaxial stress, which reduces the stress/deformation regions in the propellant grains.

An SRL has five components. These components are an insulator, a columnar material (that is, relieving the stresses), a separation sheet, a migration barrier, and a lining material intended to promote the bonding between the propellant and the insulating materials. Typically, the columns are dimensioned to provide between around 30 and 80% of nonbonded surface, the number, size, and placement being determined by stress analysis of the grains which are to be supported by the SRL.

Moving from the wall of the mold to the propellant, the SRL of this example comprises (a) a first insulator, (b) either a columnar material, or a separation sheet, (c) a second insulator, (d) an antimigration barrier and (e) a lining material. The columnar material has the form of a disk. The first and the second insulator contain the material as formulated in example 4; this formulation is modified to yield a soft columnar material based on the data of Table XI below.

<u>TABLE XI</u>

COMPOSITIONS FOR MAKING COLUMNAR MATERIALS

FROM MODIFICATIONS OF THE COMPOSITIONS OF EXAMPLE 4

Ingredients, phr	Example	4A	4B	4C	4D
Nordel 1040 (EPDM)	100.0	100.0	100.0	100.0	100.0
Varox	2.5	2.5	2.0	2.0	2.0
Cotton flocks	50.0	10.0	10.0	10.0	10.0
HiSil 233	20.0	20.0	20.0	15.0	10.0
Butarez NF	----	----	20.0	20.0	20.0

Mechanical properties

(50.8 cm/min X Head 25°C)

Parallel to the fibers

m, %	40	540	680	700	640
m, bar	44.23	48.02	33.96	27.90	30.59

Perpendicular to the fibers

m, %	----	----	650	690	680
m, bar	----	----	30.52	27.90	30.45

The tests of the materials of Table XI enabled a selection of composition 4D for the material of the support column.

The separation sheet is made of silicone elastomer (Cohrlastic[R] 9360, available from Connecticut Hard Rubber Company). Cohrlastic can vary in thickness according to the demands placed on the SRL, but the typical range is from around 0.1524 to 0.635 centimeters, for example, 0.480 cm.

Two materials were examined for making the antimigration barrier: a composition prepared per example 1 and Tuftane TF-310, a polyester-polyurethane from B.F. Goodrich. The tests show that these materials function essentially as an antimigration barrier.

The lining material is a composition as given in Table XII below:

TABLE XII

COMPOSITION OF THE LINING MATERIAL A-128A

Ingredient	Weight, %
Master batch	77.00
R-45 M (a)	65.00
Carbon black	
(FEF)	35.00
HX-868 (b)	1.50
A. O. 2246 (c)	0.15
R-45 M/TDI* (d)	21.35

* Mediator of the polymer to produce a ratio NCO:OH equivalent to 2

(a) Polybutadiene with hydroxy termination, Arco Chemical

(b) bonding catalyst, 3M Company

(c) antioxidant, American Cyanamid

(d) mixture of (a) and toluene diisocyanate from E.I. Dupont de Nemours.

Table XIII summarizes the results obtained using A-128 with the elastomeric compositions of examples 1 and 4 as mentioned above in example 5.

TABLE XIII

BONDING BETWEEN THE LINING WITH A-128 A AND PROPELLANT MG-819 (LCA-9843)*

Test temperature, °C	Tensile strength of the bond, bar			Peeling, 90 degree fold **
	$\neq 1$	$\neq 2$	$\neq 3$	
-54	44.23[a]	39.13[b]	99.42[b]	85[b]
25	12.19[b]	9.64[a]	12.19[b]	5 to 6[b]
73.8	5.65[a]	9.51[b]	6.54[a]	3.8[b]

* 88% solids with 20% of Al

** 0.508 cm/min Head X

(a) Defective especially in the lining

(b) Defective in the propellant

SRL engine, 15.24 cm

In order to verify the possibility of application of the above asbestos-free SRL system to engines with adherent propellant of terminal combustion, test engines of 15.24 cm were fabricated and tested. The fabrication involved lining a test engine of 15.24 cm with the SRL system. The method of formation of the SRL is given in Table XIV. Once the SRL is arranged in the mold, the barrier film (composition of example 1) is lined with A-128 A (Table XII) at a thickness between 0.254 and 0.381 mm. This lining is made by spraying the inside of the SRL with the A-128 A, diluted with chlorethane (2 to 1 by volume). After cladding of the lining for at least two hours at 62.77°C, a particulate propellant is poured under vacuum into the mold insulated with the SRL; the solid propellant after being poured is polymerized for 96 hours at 62.77°C. After polymerization and cool down to 25°C, an attempt was made to ventilate the SRL system; but the SRL had a length of 99.21 cm, whereas the solid only had a length of 22.86 cm, which therefore left more than 2.54 cm of SRL beyond the extremities of the

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solid. The contraction of the solid was not sufficient to separate the overreaching extremities of the SRL and accomplish the ventilation.

An attempt was made to cool down to -40°C to bring about a sufficient contraction, but this also proved ineffective. Finally, radial notches were cut in the insulating layer of the SRL, going down toward the separation sheet; the notches (6.35 mm x 5.08 cm) were situated approximately 6.35 mm from the rear end of the solid and 12.7 mm from its front end; they were spaced radially by around 2.54 cm; the notching process made possible the desired ventilation. It is easily possible to pass dry nitrogen through the SRL (from back to front) at 1.0342 bar.

After X-raying the solid to detect defects, the rear extremity is inhibited with a 9.52 mm layer of inhibitor (cf. Table XV), which is allowed to polymerize one full night (16 hours) at 25°C. An ignition disk of 25 g containing 25 g of pyrotechnic substance is attached to the rear surface of the solid and then the engine assembly is finished by securing the front head and the base to the engine.

An examination after firing reveals a uniform destruction over the inhibitor at the rear. The insulation remained intact, at the columns and the separation sheet, and even at the rear end of the layer of SRL.

TABLE XIV

METHOD OF FORMING THE SRL IN A TEST ENGINE OF 15.24 CM

1. Sandblast the interior of an engine mold – cleaning with 1,1,1-trichloroethane

2. Apply a first coat of Chemlok 233

3. Bring the Chemlok 233 up to 25°C for at least 30 minutes

4. Surround the inflatable mandrel with a layer of 0.762 cm of a composition prepared per example 4

5. Put the layer of step 4 in the cold state inside the engine mold by using a nitrogen pressure of 6.8948 bar in the bladder

6. Place the perforated silicone separation layer on the layer of step 5

7. Fill the perforations of the separation layer with disks of composition 4D (Table IX) (disks 1.27 cm in diameter and 0.508 cm in thickness)

8. Surround the inflatable mandrel with a layer of 0.812 mm thickness of the composition of example 1, then with two layers of 0.635 mm thickness of the composition of example 4

9. Place the bladder thus surrounded into the engine mold; apply a nitrogen pressure of 6.8948 bar

10. Polymerize under pressure for 2 and a half hours at 177°C.

11. Remove the mandrel

12. Sandblast the interior layer 8 prepared with the composition of example 1

13. Polymerize for 9 hours at 121°C

TABLE XV

COMPOSITION AND PROPERTY OF THE INHIBITOR

Ingredient	phr	Weight, %
R-45 M[a]	100.000	29.795
IDP (Isodecyl pelargonate)[b]	25.000	7.449
Mannitol	200.000	59.591
HX-868[c]	2.500	0.745
HMDI[d]	6.600	1.966
A. O. 2246[e]	1.500	0.447
FeAA[f]	0.025*	0.007
		100.000

Mechanical properties

Test temperature	m, %	m, bar	E, bar
-54 °C	144	38.44	119.19
-42.77 °C	127	24.94	87.50
25 °C	107	6.06	20.94
76 °C	51	5.30	17.50

Thermal expansion, in./in./°C 21.7×10^{-5}

* The content of FeAA can be adjusted to maintain the content of the product

(a) Polybutadiene with hydroxy termination from Arco Chemical and Co.

(b) Plasticizer from Emery Industries

(c) Bonding agent, 3M Company

(d) Isocyanate from Mobby Chemical Company .

(e) Antioxidant from American Cyanamid

(f) Ferric acetyl acetonate

EXPERIMENTAL SECTION

The uniaxial mechanical properties of the insulators of example 5 were determined by the method ASTM D412-68. The tests were performed on a dynamometer Instron Tensile Tester, with a speed of 50.8 cm/minute. The mechanical properties of the propellant were determined on specimens of type Class "C" with an effective length of 6.86 cm; the test temperatures and the rates of deformation varied according to the duration/temperature response spectrum.

Triaxial dynamometric tests were carried out using samples of 10.16 cm. These samples had a column diameter of 1.27 cm by 0.477 cm length. The surface of the column was maintained at 50% of the total SRL bonding surface. The tests were carried out at two temperatures and different rates of deformation to furnish data for the stress analysis.

The data on the traction and peeling relationship at 90°C were obtained by stretching appropriate specimens on an Instron dynamometer at speeds of 0.508 cm/min.

The samples were triaxial samples of 3.81 cm diameter (buttons), containing layers of insulator and propellant. The peeling samples were propellant blocks of 2.54 cm width (2.54 x 2.54 x 7.62 cm), the insulator being bonded to one of the surfaces. The bonding was done by pouring and polymerizing the propellant on reinforced glass panels of insulators, lined (with A.128 A) (15.94 x 15.24 cm).

CLAIMS

1. Elastomeric insulating material free of asbestos for rocket engine, containing a cross-linked elastomeric polymer and carbonizable organic fibers, characterized in that the organic fibers are cotton flocks, sisal, or a combination of cotton flocks and sisal, and the quantity of organic fibers is between around 10 and around 100 parts by weight per 100 parts by weight of elastomeric polymer.

2. Elastomeric insulating material free of asbestos per claim 1, characterized in that the quantity of organic fibers is between 15 and 75 parts by weight per 100 parts by weight of elastomeric polymer.

3. Insulating material per claim 1, characterized in that the organic fibers are primarily cotton flocks.

4. Insulating material per claim 3, characterized in that it contains between around 20 and around 60 parts by weight of cotton flocks per 100 parts by weight of elastomeric polymer.

5. Insulating material according to any of claims 1 through 4, characterized in that the elastomeric polymer is essentially comprised of ethylene propylene diene (EPDM).

6. Insulating material according to any of claims 1 through 4, characterized in that the elastomeric polymer is essentially comprised of chlorosulfonated polyethylene.

7. Insulating material according to any of the preceding claims, characterized in that it contains between 5 and 80 parts by weight of silica per 100 parts by weight of elastomeric polymer.

8. Insulating material per claim 1, characterized in that it contains up to 30 parts by weight of silica per 100 parts by weight of elastomeric polymer.

9. Insulating material per claim 8, characterized in that it contains up to 20 parts by weight of silica per 100 parts by weight of elastomeric polymer when the quantity of organic fibers is not more than 50 parts by weight per 100 parts by weight of elastomeric polymer.

10. Insulating material according to any of the preceding claims, characterized in that it contains up to 60 parts by weight of antimony oxide per 100 parts by weight of elastomeric polymer.

11. Insulating material per claim 10, characterized in that it contains between 10 and 80 parts by weight of a chlorinated organic compound per 100 parts by weight of elastomeric polymer.

12. Insulating material per any of the preceding claims, characterized in that it contains up to 150 parts by weight of a particulate phenolic resin per 100 parts by weight of elastomeric polymer.

13. Insulating material per any of the preceding claims, characterized in that it contains up to 50 parts by weight of liquid polybutadiene.